

ATMOSPHERIC SULFUR BEHAVIOR IN POWER PLANT AND REGIONAL PLUMES*

Rudolf B. Husar
Air Pollution Research Laboratory
St. Louis, Missouri

INTRODUCTION

A key question in the current energy debate concerns the economic and environmental costs of increased coal usage as a replacement for gas and oil. The environmental constraints are due to mining, transportation, and the release of combustion products (SO_x , NO_x , CO_2 , and fly ash). Sulfur oxide emissions and their effect on the environment have been under intense study during the past 25 years, first because of the acute air pollution episodes that occurred in populated areas (e.g., the 1952 and 1962 London episodes) and more recently because of the chronic effects on the ecosystem (e.g., acidification of lakes in southern Scandinavia and the Northeastern United States).

The past years of monitoring and research have contributed appreciably to the understanding of atmospheric sulfur behavior. The key findings are summarized in the following sections.¹

Sources

The emission rate of sulfur dioxide (SO_2) in the United States from man-made sources was 32×10^6 metric tons/year in 1973 (U.S. Environmental Protection Agency (ref. 1)), or about 0.5 kg of SO_2 per person per day. Fuel combustion accounted for 80.1 percent, while industrial processes (metal, petroleum, and chemical manufacturing) contributed 17.9 percent and transportation 2 percent to the national SO_2 emissions (fig. 1). Of the fuels used by utility and industry, coal contributed 65 percent and oil 13 percent. About 75 percent of the SO_2 is emitted east of the Mississippi River with the highest emission density in the area of the Ohio River Valley (fig. 2). Within this region, fuels accounted for 92 percent of the total SO_2 emissions. West of the Mississippi River (25 percent of the national SO_2 emissions), 62 percent of SO_2 was due to mining and industrial processes and 38 percent to fuels.

Sulfur compounds are also emitted from natural sources, for example, sea spray and decomposition of organic materials. Globally, natural emissions are

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estimated to be comparable with man-made sulfur emissions (Granat et al. (ref. 2)), but over regional scales (e.g., northern Europe), it is concluded that man-made sources dominate the sulfur budget (Rodhe (ref. 3) and International Symposium on Sulfur in the Atmosphere (ISSA) Workshop (ref. 4)).

SO₂ and Sulfate Concentrations

Currently, a solid historical data base exists for the SO₂ levels in urbanized areas of the United States and shows a decline from an annual average of 38 µg/m³ in 1970 to 26 µg/m³ in 1974. The annual mean sulfur dioxide standard of 80 µg/m³ was only exceeded in 1974 at 31 out of 1030 stations (3 percent). The 24-hour SO₂ standard was exceeded at 5 percent of the reporting stations. In the 1960's, high SO₂ concentrations were recorded within large urbanized areas and those show the strongest reduction of SO₂ concentrations. In smaller cities, the concentrations have remained essentially constant for about the past 5 years, at about 18 µg/m³ (U.S. Environmental Protection Agency (ref. 1)).

The historical data base for sulfate (SO₄²⁻) concentrations is less satisfactory. Inspection of the existing data (Frank and Possiel (ref. 5)) reveals decline of sulfate in large metropolitan areas and an upward trend over the past 10 years in rural and small urban areas. Over 90 percent of the National Air Surveillance Network (NASN) monitoring sites are located in urbanized areas, while the emissions have been shifting away from central city locations and are now emitted from taller stacks. Thus, the overall strong decline of SO₂ concentrations and the more or less constant sulfate levels are most likely due to the redistribution of source location and emission height. This speculative argument is currently under study by both governmental and industrial research teams.

Transformations

The primary pollutant, SO₂, is subject to chemical reactions in the atmosphere which lead to a change in the oxidation state, most commonly to SO₄²⁻. The reactions are accompanied by gas-particle conversion having as the end product particulate sulfur which is a secondary pollutant.

Evidence is accumulating that the effects of sulfur oxides (e.g., on terrestrial and aquatic ecosystems, health, visibility, weather and climate modification, material damage) are associated with the reaction products rather than with SO₂ itself. For this reason, an appreciable fraction of current sulfur research is focused on the SO₂ transformations. The questions of main concern pertain to (1) the mechanism and rate of conversion, (2) the fraction of SO₂ transformed to sulfate, and (3) the chemical and physical properties of the particulate sulfur.

It is the current understanding that the oxidation of SO₂ without the presence of interfering compounds is slow compared with the observed or inferred atmospheric conversion rates. Hence, the current challenge of atmospheric

chemistry is to determine which substances and environmental or emission parameters promote or inhibit SO_2 oxidation in the atmosphere.

From the point of view of effective controls, the specific questions are

(1) Is the aerosol formation rate linearly proportional to SO_2 concentration? If so, "linear rollback" control strategies will work as expected; a cutback in SO_2 emissions will lead to a proportional reduction of sulfates. It is conceivable, however, that the conversion rate is dominated by external parameters and is only weakly dependent on SO_2 . In that case, large reductions of SO_2 would yield only marginal improvement in sulfate levels.

(2) Are the oxidizing agents of SO_2 man-made and can they be controlled? If SO_2 oxidation is promoted by man-made oxidizing agents (as it is now suspected), then the specific role of those substances (e.g., the HO radical) should be established and the means of their control should be explored.

(3) Do natural (e.g., meteorological) parameters influence the SO_2 conversion? Temperature, humidity, solar radiation, or any other natural parameter may influence the conversion rate and offer a possibility of supplemental controls.

(4) What is the chemical composition of the particulate sulfur? Acidic aerosol is believed to be environmentally more harmful than neutral aerosol. The conditions that favor acid aerosol formation should be established.

In order to answer these questions, an understanding of the SO_2 conversion mechanisms is necessary. Following is a brief account of the current understanding of the subject. There are four mechanisms which are believed to be of significance for atmospheric SO_2 conversion.

Indirect photooxidation is a major route for SO_2 -to-sulfate conversion in the troposphere. The SO_2 is oxidized following gas-phase collision with strong oxidizing radicals such as $\text{HO}^\cdot$, $\text{HO}_2^\cdot$, and $\text{CH}_3\text{O}_2^\cdot$. The sources of these radicals in the polluted troposphere are hydrocarbon- NO_x emissions, which in the process of daytime photooxidation produce oxidizing radicals as intermediate products. The SO_2 oxidation step is therefore indirectly linked to photochemistry. The chemical kinetics of this mechanism has been formulated in models using measured rate constants (Calvert et al. (ref. 6)). The modeling results were consistent with laboratory tests of SO_2 conversion in the presence of photochemically reacting hydrocarbon- NO_x mixtures (Miller (ref. 7)). An unambiguous confirmation of the homogeneous conversion mechanism would require the direct observation of the reactive intermediates ($\text{HO}^\cdot$, $\text{HO}_2^\cdot$, $\text{CH}_3\text{O}_2^\cdot$, etc.) under a variety of atmospheric conditions. Currently, such data are not available.

Numerical simulations of chemical kinetics for typical urban mixtures (fig. 3) indicate 2 to 4 percent/hour for sunny summer days (Calvert et al. (ref. 6)). Eggleton and Cox (ref. 8), in a summary of European results, conclude that in the western European summer, SO_2 oxidation rates due to gas-phase radical reactions in sunlight are expected to be between 0.5 and 5 percent/hour, depending on the degree of pollution of the atmosphere. The

lower figure refers to a cleaner troposphere. In the winter, because of the reduced sunlight intensity and duration, the conversion rates are expected to be slower by at least a factor of 2 to 5.

Smog chamber measurements occasionally show higher conversion rates (Miller (ref. 7)). It is likely that the homogeneous conversion rate will depend on the absolute concentration as well as on the initial ratio of hydrocarbons to NO_x .

The specific roles of temperature, dew point, solar radiation, solar intensity, and so forth in the indirect photooxidation require systematic future studies. The current understanding is sufficient, however, to incorporate gas-phase chemistry into large-scale reactive plume models.

Catalytic SO_2 oxidation in droplets has been studied extensively, but the results regarding its role in the atmosphere are less conclusive. The consensus at the International Symposium on Sulfur in the Atmosphere in Dubrovnik, Yugoslavia, was as follows (ref. 4):

"The catalyzed oxidation of SO_2 in solution by transition metals (e.g., Fe, Mn) is believed to be important in situations in which relatively high ($>10^{-5}$ M) concentrations of catalyst are present in the droplet and in which the total atmospheric concentrations of catalytic elements are also high. Such conditions can exist in urban and stack plumes and perhaps in urban fogs. In cleaner rural air this reaction would occur only in clouds. However, unless the pH and metal concentrations in cloud water are substantially different from those in rain water, this process is unlikely to be of significance. Both laboratory and field studies of such reactions are necessary."

Oxidation in the liquid phase by strong oxidants has recently been receiving increasing attention (Eggleton and Cox (ref. 8) and Beilke and Gravenhorst (ref. 9)). Ozone and H_2O_2 absorbed in liquid droplets can promote the oxidation rate to be comparable with or exceed the indirect photooxidation rate. However, the current oxidation rate data vary by 2 orders of magnitude which prohibits an assessment of its importance in the atmosphere. The ozone and H_2O_2 in polluted atmosphere also originate from the gas-phase photooxidation of hydrocarbon- NO_x mixtures. Within clouds or fogs, such gases are absorbed into the water droplets within seconds. Measurements of H_2O_2 in polluted and clean atmosphere are necessary as well as chamber studies to resolve the discrepancy of existing laboratory data.

Surface catalyzed oxidation of SO_2 upon collision with solid particles has been demonstrated in the laboratory. Elemental carbon (soot) appears to be particularly effective in this regard (Novakov et al. (ref. 10)). However, since the existing data refer to SO_2 oxidation on filters containing soot, the importance of this mechanism for suspended aerosol formation cannot be assessed quantitatively.

Common features of the major SO_2 conversion mechanisms discussed are that (1) the rate-controlling species can be identified, (2) they may, in principle, be controlled independently from SO_2 , and (3) their source is not necessarily

that of the SO_2 . It is regrettable that currently only the indirect photo-oxidation mechanism can yield SO_2 oxidation rates, and therefore one cannot evaluate the relative importance of each mechanism. A major difficulty with the interpretation of laboratory liquid-phase reaction results is that in the atmosphere that reaction probably occurs in events (clouds) rather than continuously.

Removal

The residence time and the transport distance of sulfur are essentially determined by the overall removal rate of sulfur compounds from the atmosphere. The overall removal has four major components: dry removal of SO_2 , wet removal of SO_2 , dry removal of SO_4^{2-} , and wet removal of SO_4^{2-} . Dry removal of SO_2 and wet removal of SO_4^{2-} appear to be the two major components.

Dry removal is a mass transfer process whereby SO_2 is first transported to surfaces by turbulent and molecular diffusion and then removed by adsorption or absorption at the surface. The overall mass transfer rate can be characterized by a mass transfer coefficient (v_d) and the difference between the bulk and surface concentrations. Since the units of v_d are length per time, it is called "deposition velocity." Conceptually, it is also convenient to utilize the overall resistance to mass transfer $r = 1/v_d$, which is the sum of several, largely independent resistances.

The ranges of deposition velocities were summarized at ISSA in Dubrovnik, and are given in table I.

The surface resistance (r_s) incorporates adsorption and absorption. In case of vegetation, r_s is believed to be dominated by the size of the stomatal openings. The aerodynamic resistance (r_a) is due to turbulent diffusion in the atmospheric surface layer and controls the dry deposition rate during stable (inversion) conditions.

Wet removal of sulfur compounds proceeds through the collection of material into cloud droplets and the subsequent deposition in rain. The wet removal rate, therefore, can be estimated from the sulfur content and the rate of rainfall. Table II summarizes the current estimates of wet and dry deposition rates.

Wet and dry removal rates are evidently of comparable magnitude, dry deposition dominating the SO_2 removal (about 60 percent of the total) and wet deposition dominating the SO_4^{2-} removal (40 percent). Both removal processes limit the lifetime of sulfur compounds to 2 to 3 days (Workshop (ref. 4)).

The residence time of the sulfur dioxide is determined by the competing rates of transformations to sulfate and of removal of SO_2 and SO_4^{2-} . Taking a conversion rate of 1 to 2 percent/hour and an overall removal rate of 2 to 5 percent/hour leads to a characteristic residence time of 14 to 33 hours or about 1 day for SO_2 .

The residence time of sulfate is the sum of the formation and removal times. According to the current estimates (Workshop (ref. 4)), the sulfate residence time is between 3 and 5 days.

Sulfur Transport

The concentrations and the fate of atmospheric sulfur are influenced by meteorology through the horizontal and vertical transport mechanisms. Horizontal transport characterized by the wind speed field provides dilution and "long-range transport"; the turbulent eddy exchange in the vertical direction disperses the matter within the mixing layer and delivers the pollutants to the surfaces for the dry deposition. The mixing of plume material with the potentially reactive background air is facilitated by both horizontal and vertical dispersion.

The characteristic residence time is on the order of 1 day for SO₂ and about 1 week for sulfate. A typical transport speed in the planetary boundary layer (1 km) is about 500 km/day; hence, the transport distances are on the order of 500 km for SO₂ and 3000 km for sulfate. The meteorological framework in which sulfur transport needs to be considered is therefore over the synoptic scale. The recognition of this fact leads to the strong current interest in the long-range transport (OECD (ref. 11) and Ottar (ref. 12)), specifically to the question of sulfur transport across national boundaries.

FIELD OBSERVATIONS OF SULFUR BEHAVIOR

Laboratory studies of sulfur transformations (smog chamber and bucket experiments) and of dry and wet removal generally are designed for a systematic parameter by parameter examination of these processes. The utility of these studies is that they may elucidate the possible atmospheric mechanism and rates. The burden of establishing the actual mechanism and rates falls upon the field experiment.

Field observations may be conducted over the mesoscale range (about 100 km) or on the regional scale (about 1000 km). Both the experimental approach and the obtained results are quite different for mesoscale and regional studies.

Regional-Scale Monitoring and Modeling

In this approach, an emission inventory over a region and meteorological transport parameters are used as inputs to regional-scale (order of 1000 km) transport models. The models also incorporate the rates of SO₂ conversion and removal. The actual rate constants are unknowns but they can be extracted from a best fit comparison between calculated and observed values. In the OECD study of Long-Range Transport of Air Pollutants (ref. 11), the trajectory models were tuned to monitoring data obtained daily at about 70 (European) stations. The measured daily concentration data for SO₂, SO₄²⁻, and SO₄²⁻ in precipitation were compared with calculations, and the rate constants for transformations and

dry and wet removal were adjusted until a best fit was obtained. The key model parameters for the OECD study are listed in table III.

The year-round average conversion rate of 1 to 2 percent/hour and the overall average dry removal rate of about 3 to 4 percent/hour are key new results of the OECD study. Studies similar in scope and objectives to the OECD study are being conducted in the United States. The Sulfate Regional Experiment (SURE) (Perhac (ref. 13)) by the Electric Power Research Institute, the Multistate Atmospheric Power Production Pollutant Study (MAP3S) (MacCracken (ref. 14)) by the Department of Energy, and the Sulfur Transport and Transformations in the Environment (STATE) (Robinson (ref. 15)) by the Environmental Protection Agency are examples of projects.

The main utility of the regional approach is that the obtained rate constants are inherently averages over all sources and spatial-temporal scales of interest. It is recognized, however, that the rate constants for removal and transformations are actually variables which may depend on source configuration, meteorological parameters, and external (non-sulfur) species present.

A pictorial illustration of long-range transport is given in figure 4 (Husar et al. (ref. 16)). Contour maps of noon visibility outline the spatial extent and temporal changes of a hazy air mass over the eastern half of the United States. Inspection of the sequence of contour maps reveals that during the 2-week period, multistate regions were covered with the haze layer in which the noon visibility was less than 9.6 km. Long-range trajectory calculations and evaluation of surface wind data from the weather stations indicate that the hazy air mass located south of the Great Lakes (June 25 to 27) entered the continental United States in Louisiana and moved northward somewhat east of St. Louis. The air movement directions were also checked by surface wind directions obtained at the weather stations.

During June 28 to 30, the "blob" drifted slowly westward under easterly winds, passing over St. Louis, Missouri, on June 28 and 29 and then continuing across Missouri, Kansas, Iowa, and Minnesota for the next 2 days (July 1 and 2). Starting on July 3, the hazy air mass was transported to the southeast corner of the continental United States by a southward-moving Canadian front. By July 5, the hazy air mass caused visibility deterioration of less than 6.4 km over Atlanta, Georgia, Birmingham, Alabama, and Tallahassee, Florida.

The daily weather charts for the period from June 29 to July 4, 1975, are shown in figure 5 (Husar et al. (ref. 16)). A major feature of the weather system during that period was the tropical storm Amy, located off the northeast coast. By its presence, the tropical storm provided a barrier against large-scale eastward motion. From the northwest, a front was approaching the Great Lakes. With the advance of the Canadian front toward the southwest, the high-pressure zone located between the front and the tropical storm Amy drifted slowly to the southwest, passing over Missouri on July 2 and 3. By July 4, the front itself reached Missouri.

The two passages of the blob over St. Louis, Missouri, are confirmed by the two peaks (June 27 to 29 and July 2 to 4) of the light scattering coefficients (b_{scat}) measured locally with integrating nephelometers (fig. 6(a)). A

similar temporal pattern may be observed (fig. 6(b)) for the extinction coefficients (b_{ext}), based on visibility observations in St. Louis, Missouri, and in Springfield, Illinois. The similarity of b_{scat} and b_{ext} patterns at distant monitoring points confirms that the major changes in the light scattering and extinction coefficients during this case study have spatial scales substantially larger than the St. Louis metropolitan area. Also, these observations confirm that the light scattering aerosol is the result of external inflow, rather than the result of local source contributions. The correlation between b_{scat} and b_{ext} shown in figure 6 demonstrates the utility of visibility observations as a qualitative surrogate for measurements of the light scattering aerosol concentration.

The daily average sulfate concentrations using high-volume filters were measured before, during, and after the passage of the hazy air mass over St. Louis, Missouri. High-volume filter samples, collected every 6 days by the St. Louis County Department of Health, were analyzed for particulate sulfur by using the flash volatilization-flame photometric detection method (Husar et al. (ref. 17)). An increase from $9.2 \mu\text{g}/\text{m}^3$ on June 23 to $32.7 \mu\text{g}/\text{m}^3$ on June 29 is shown in figure 6. The sulfate content then dropped to $8.0 \mu\text{g}/\text{m}^3$ on July 5 after the passage of the Canadian front. Sulfate accounted for 19 percent of total aerosol mass before, 34 percent during, and 15 percent after the passage of the hazy air mass. The daily average sulfate concentrations were compared with daily average b_{ext} (uncorrected for relative humidity effects) for the entire summer (June, July, and August 1975). The correlation coefficient was found to be $r = 0.7$ and the regression equation for 16 points was $b_{ext}(10^{-4}\text{m}^{-1}) = 3.24 + 0.11[\text{SO}_4^{2-}](\mu\text{g}/\text{m}^3)$. These results tend to suggest that a substantial fraction of the haze aerosol, particularly during the passage of blobs, is associated with sulfates.

This brief analysis of national visibility data, local air pollution data, and synoptic air parcel trajectories points toward two intriguing phenomena. First, multistate-scale haziness may be caused by long-range transport from sources 1000 km or more away, and secondly, the haze aerosol ($<1 \mu\text{m}$ in diameter) in such air masses is largely composed of sulfates.

By inspection of visibility contour maps for June, July, and August 1975, the author has identified six blobs with an average residence time of 8 days over various multistate regions of the midwestern and eastern United States. In the St. Louis metropolitan area, the hazy air masses were accompanied by high midday ozone concentrations, generally exceeding the ambient air quality standard of 0.08 ppm.

Establishing the spatial distribution and the movement of hazy air masses is only the first step toward the understanding of their characteristics and their impact on human health and welfare, on weather and climate, and on other aspects of the ecosystem. The remaining major questions pertain to the sources of hazy air masses (both anthropogenic and natural), to gaseous precursors of haze particles, to the environmental conditions which promote their development, and to the fate of such hazy air masses.

Mesoscale Plume Studies

The average rate constants for transformation and removal may be obtained from the regional monitoring and modeling efforts. However, the specific dependence of the rates on the underlying chemical and physical processes has to be studied on a smaller scale. The gap between regional-scale (1000 km) and laboratory simulation can be bridged by mesoscale studies of sulfur transport, transformations, and removal (transmission). These are generally referred to as plume studies. Inherently, quantitative single plume studies are limited to a spatial scale of less than 500 km and a plume age below 12 hours.

The results of a 4-year plume mapping study (Midwest Interstate Sulfur Transformation and Transport (MISTT): Wilson (ref. 18)) conducted in St. Louis, Missouri, on the Labadie power plant (2400 MW, 6 kg/sec sulfur output, and 218 m stack height) show that the transport, transformations, and removal processes in power plant plumes all have diurnal cycles (fig. 7).

Transformations.— The daytime conversion rate was observed to be quite variable, between 1 and 4 percent/hour, while the nighttime values were consistently below 0.5 percent/hour (Husar et al. (ref. 19)). Hence, in the midwestern United States, during summer, the conversion-rate-controlling parameter was associated with the time of day. The data were insufficient to conclude which mechanism controlled the daytime conversion because the observed variation was consistent with indirect photooxidation as well as with liquid-phase oxidation in clouds. Observations of aerosol size spectrum dynamics in plumes (Whitby et al. (ref. 20)) have shown, however, that homogeneous nucleation occurred consistently. Gillani et al. (ref. 21) noted that the aerosol formation in the same plumes is frequently accompanied by ozone formation within the plume. Both of these observations would support homogeneous indirect photooxidation. However, in summer in the St. Louis region, the plume material is transferred through clouds at least once on most days. Hence, the estimation of the relative contributions of homogeneous and heterogeneous chemistry is not possible at this time.

Horizontal transport.— The speed at which plume material is transported over a given location is a function of both height and time. For the St. Louis region, the Regional Air Pollution Study (RAPS) provides an extensive data base for the time-height dependence of wind speed and direction as well as temperature and dew point (Myers and Reagan (ref. 22)). The average vertical profiles of wind speed and their standard deviation from July 1976, are shown in figure 8(a). Vertical velocity soundings at 1300 CDT show on the average a uniform speed of 4 to 5 m/sec up to about 1000 m. Hence, the noon wind speed within the planetary boundary layer is less than the geostrophic wind speed (6 m/sec) above, because of the drag of buoyant thermals. At 1900 CDT, there is evidence of an increase in speed between 300 and 600 m which becomes more pronounced at 0100 CDT. The peak average speed of 12 m/sec is recorded at 450 m, with a strong vertical shear near the ground and a weaker shear layer between 450 and 1200 m. The high wind speed at 450 m is called a low-level jet, and it is illustrated in more detail by Smith et al. (ref. 23). By 0700 CDT, the vertical profile has become more homogeneous at reduced speeds, with the exception of the lowest 200 m, which is already subject to drag from the nascent mixing layer. The diurnal pattern of the wind speed obtained from

hourly averages at seven heights is shown in figure 8(b). The ground-level (10 m) wind speed is obtained from RAPS surface measurements. The figure illustrates that within the diurnal cycle in the St. Louis region, nighttime plume transport is greater than at midday by a factor of nearly 2. Nocturnal plumes emitted from tall stacks are affected by 10 to 20 m/sec low-level jets in two ways: their effective stack height is reduced because of the crosswind, and the distance traveled overnight is increased to as much as 500 km. Since such plumes are subject to minimal vertical mixing, aircraft sampling is feasible up to several hundred kilometers.

In addition to the longitudinal and vertical transport, plume dispersion also occurs by "veer," that is, wind directional change with height. The vertical profiles of veer for a given hour were obtained by taking the absolute value of the directional change per 100 m. Of the four profiles shown in figure 8(c), the 1400 CDT readings showed the least average veer. Evidently, the vigorous daytime mixing inhibits the development of such lateral dispersion. Soundings at 0400 CDT exhibited the strongest veer effects near the surface, supporting the notion that the low-level nocturnal jet is decoupled from the surface stable layer.

Therefore, while transformation has been shown to be a daytime mechanism, the long-range transport in the midwestern United States is primarily a nocturnal phenomenon.

Vertical transport.- Pollutants are delivered by turbulent mass transfer from the plume height to the roughness height of the canopy level, where dry deposition takes place. During the daytime, the lower levels of the atmosphere are heated by the warmer surface causing convective mixing between the surface and an inversion layer, sometimes referred to as the lid of the mixed layer. The height of the mixed layer has a characteristic diurnal pattern. For the St. Louis region, this pattern is illustrated in figure 7(a), which shows that the mixed layer height rapidly increases from near ground level in the morning to 1000 m at noon and then levels off at about 1200 m by midafternoon. At night, the convective mixing tends to die out because of the development of a cold stable air layer near the ground. The former mixed layer becomes thermally stratified and pollutants tend to remain in the strata into which they were introduced.

In the afternoon, the low wind speed and slight instability of the mixed layer permit thermally buoyant plumes to rise without appreciable transport or dilution up to the inversion layer, which usually persists at 1000 to 1500 m. The large effective stack height of afternoon buoyant plumes has important consequences regarding sulfur transformations and removal, that is, the sulfur budget.

The rise of thermals above cities, industrial areas, and power plants is well documented in the "heat island" literature. In St. Louis, development of thermals has been frequently observed over the Wood River refinery complex, causing industrial cumulus formation sometimes penetrating the inversion layer (e.g., Auer (ref. 24)). Similar cumulus formation has also been noted over the 2400-MW Labadie power plant. It is recognized that such cloud formation is

only possible under light wind conditions. The average wind speed in the mixed layer during the convective hours is between 4 and 5 m/sec (fig. 8(b)). When there is an appreciable wind, the rising buoyant plume is bent in the direction of the wind flow and reaches the top of the mixed layer without penetrating it. The dilution of such a plume is minimal, and it persists overnight as "convective debris" (Edinger (ref. 25)) at 1000 to 1500 m. Hence, the plume center line is just below the upper inversion lid. Such a plume will remain in an elevated stratified layer until the next day when the rising mixing layer reaches the plume.

There are two consequential phenomena of the diurnal vertical plume transport pattern worth emphasizing: (1) the decoupling of the daytime mixed layer from the underlying surface via the nocturnal inversion, and (2) the lifting of late afternoon plumes which remain in high strata at least until the following noon when they may or may not be entrained in the mixing layer.

Dry removal.— Unlike the field measurement of sulfur transformation which has a measurable product in the form of particulate sulfur, the estimation of removal rates is inherently more difficult. Removal rate is obtained from the difference between total sulfur (S_t) at two heights (gradient method) or at two plume ages (plume budget method). The difficulties which appear in practice in such estimates arise from taking the difference of two values of comparable magnitudes, each with uncertainties comparable with the difference. This is particularly true for elevated plumes emitted from tall stacks, where removal is often not appreciable for the first several hours of plume age. This necessitates the combined use of deposition velocity estimates, ground-level concentration data in the vicinity of power plants, and sulfur budget data from plume mapping experiments, as described by Husar et al. (ref. 19).

TWO-BOX MODEL OF THE SULFUR BUDGET IN LARGE PLUMES

The essence of the previous considerations of dispersion is that the plume has two distinctly different regimes during the diurnal cycle. The first regime develops when the plume is decoupled from the underlying surfaces by radiation inversion or by other stable strata. In this regime, material is lost by entrainment into a second mixing-deposition regime. In the second regime, the plume is dispersed rapidly within the mixed layer, loses material at the surface, and gains material by entrainment from above. Conversion of gaseous sulfur to particulate sulfur occurs in each regime. During its lifetime, the plume sequentially passes through these two regimes every day, as illustrated schematically in figure 9.

For estimating the sulfur budget in a plume passing through the diurnal cycle, it is instructive to describe the system in terms of a "two-box model." The sulfur budget at any given time can then be obtained by carrying out the mass balance in each of the boxes. Box I shall be the quiescent "aging reservoir," decoupled from the surface. The mass balance equation for gaseous sulfur S_g and for particulate sulfur S_p in box I can be written as follows:

$$\frac{d}{dt} S_g^I = - \frac{1}{H'} \frac{dH}{dt} S_g^I - k_t S_g^I$$

$$\frac{d}{dt} S_p^I = - \frac{1}{H'} \frac{dH}{dt} S_p^I + k_t S_p^I$$

where t is time, H is the mixing layer height, H' is the difference between the maximum mixing layer height and H , and k_t is the transformation rate constant. The first terms on the right-hand sides of the equations signify the transfer of material from box I to box II due to the rising mixed layer height. The second terms are the conversion terms.

The material balance for the mixing-transformation-removal box II can be written as follows:

$$\frac{d}{dt} S_g^{II} = \frac{1}{H'} \frac{dH}{dt} S_g^I - k_t S_g^{II} - d_g S_g^{II}$$

$$\frac{d}{dt} S_p^{II} = \frac{1}{H'} \frac{dH}{dt} S_p^I + k_t S_p^{II} - d_p S_p^{II}$$

The terms involving the dry removal rate constants d_g and d_p are the dry removal terms for gaseous and particulate sulfur, respectively (Husar et al. (ref. 19)).

During the nighttime, elevated plumes are emitted into the reservoir box and reside there until entrainment into the next day's mixed layer. Daytime emissions are also held in the reservoir box for a characteristic "mixing time," following which perfect mixing is assumed. All plume material is then transferred into the mixing-transformation-removal box (fig. 9). At 1800, the collapse of the mixing height, followed by the decoupling of the surface layer from the former mixed layer, is interpreted as a "catastrophe." The consequence of this abrupt transition is to transfer the bulk (90 percent) of the plume material back into the reservoir box. A token amount (10 percent) of the material is retained in the mixing-transformation-removal box of the nocturnal mixing layer and is subject to dry deposition. By morning, the stable layer near the ground is nearly depleted of SO_2 , while the mass in the reservoir is conserved. At 0600, the rising mixed layer starts to entrain material from box I to box II and subjects an increasing amount of matter to dry removal. By late afternoon, practically all material has been transferred to the mixing box II, followed by a repeat of the catastrophic transfer from box II to box I at 1800.

The gaseous and particulate sulfur contents of the two boxes are displayed in figure 9 for a 4-day period following emission. The foregoing kinetic process may be envisioned in terms of a "two-bucket analogy," in which the reservoir bucket, box I, is connected to a mixing-transformation-removal bucket, box II, through a pipe regulated by a valve which represents entrainment. Bucket II has a porous bottom, reflecting dry removal at the surface. The contents of the reservoir bucket are slowly transferred to bucket II which through its porous bottom loses about 40 percent of its contents during the first day. At 1800, the remaining contents are poured back into the reservoir and the process repeats itself.

The plume sulfur budget is obtained by combining the gaseous and particulate sulfur content of both boxes to get the total amount converted to S_p and that remaining as S_g . Such sulfur budgets are shown in figure 10 for four release times. In the budget figures, the dotted upper portion represents the cumulative percent of aerosol formed. The lower hatched area stands for the cumulative fraction of removal by dry deposition. The open area in between is the gaseous sulfur remaining in the atmosphere. For each of the four emission types, both aerosol formation and dry removal occur in daily waves with peak effects during the daylight hours. Overall, however, the SO_2 decay resembles that of an exponential function.

It is recognized, of course, that the model results can be no better than their input. Nevertheless, the consequences of the previously derived diurnal pattern of plume dispersion, transformation, and removal upon the calculated sulfur budget will be examined next. The most intriguing is the afternoon emission at 1600 CDT. The plume leaving the stack rises to nearly 1000 m and undergoes some transformation (10 percent) without removal overnight. It is not until noon the next day that the plume is entrained into the mixed layer, and by that time about 16 percent of the original sulfur mass has already converted to S_p form. Following entrainment in the mixed layer, the S_g decay is roughly exponential; about half of the decay is due to transformation and half to removal.

The 2200 CDT emission is also emitted into a stable, but lower, stratus and is therefore mixed earlier the next morning, about 1000 CDT. In this case, as well as for the 0400 CDT emission, the transformation and removal processes have their first major impact almost simultaneously. The morning emission at 1000 CDT is injected within the mixed layer and therefore is exposed to the ground within less than 1 hour. Here again, SO_2 depletion by transformation and removal starts simultaneously.

Figure 11(a) shows the fraction of total gaseous sulfur which is converted to sulfate aerosol at plume ages of 6 hours up to 8 days. The total fraction converted ranges between 30 and 45 percent, which is attained within 8 days. For the average daily emission, about half of the ultimate particulate sulfur is formed within 24 hours after emission. The highest fraction converted (45 percent) belongs to the afternoon emissions, because of their head start in conversion. This exercise points to the late afternoon releases as most conducive to sulfate formation and provokes the thought that any reduction in the afternoon emissions would yield a most efficient sulfate reduction.

The formation time for particulate sulfur, expressed in terms of the time required to form 50 and 66 percent of the ultimate S_p (fig. 11(b)), has a characteristic value between 25 and 40 hours. There is a significant variation of the $1/e$ decay time of S_g ranging between 26 hours for the 1000 CDT emission to 46 hours for the 1600 CDT emission (fig. 11(c)). The SO_2 half-life exhibits even more variability, varying from 10 hours for the 0800 CDT emission to 38 hours for the 1600 CDT emission.

The characteristic transport distances associated with different plume ages are estimated as follows: (1) a plume height or range of heights was assigned to each hourly emission throughout its mixing history; (2) the horizontal wind speed $\bar{u}(t)$ was obtained from the RAPS data of figure 8. The travel distance is therefore a numerical integral of $\bar{u}(t) \Delta t$ from the emission time. The transport distance ($\bar{x}$) obtained is the range to which the plume would travel if the wind direction and wind speed were invariant in space; this being unlikely, the characteristic distance may at best approximate the distance traveled along a curved synoptic-scale trajectory. The calculated distances for 6, 12, and 24 hours and for $1/e$ decay time are shown in figure 11(d). The low $\bar{x}$ of 200 km at 12 hours age for 0600 CDT emissions arises from the low daytime transport velocity within the mixing layer. The plume emitted at 2000 CDT travels to $\bar{x} = 410$ km within the first 12 hours. After 24 hours of plume age, $\bar{x}$ is 600 km irrespective of emission time. From the point of view of plume impact, it is also worth estimating the distance the plume travels when SO_2 has decayed to a fraction $1/e$ of its initial value (fig. 11(d)). Because of the low $1/e$ decay time, the impact distance is about 700 km for the 0600 to 1200 CDT emissions; the distance then rises rapidly to over 1000 km for the 1400 to 2400 CDT emissions. Hence, not only does the afternoon plume appear to have higher sulfate formation, but it seems that its SO_2 impact is further away from the plant.

CONCLUSIONS OF INTERNATIONAL SYMPOSIUM ON SULFUR

IN THE ATMOSPHERE

It seems appropriate to state here the conclusions of the International Symposium on Sulfur in the Atmosphere (ISSA) as perceived by this author.

(1) Global sulfur budget: The revision of the global natural sulfur emission rate from about 100 to 30 Tg/year (Granat et al. (ref. 2)) has not been disputed at ISSA. Hence, it is the current thinking that man contributes about 60 percent of the global sulfur emissions, most of it over northwestern Europe and the industrialized part of North America (≈ 5 percent of the Earth's surface).

(2) Regional budgets: (a) Recent data show that the concentration of natural sulfur compounds over continental Europe is low compared with man-made sulfur (Georgii (ref. 26)); (b) there is a close resemblance of the airborne sulfur concentration and the man-made sulfur emission field over northwestern Europe (Ottar (ref. 12)); (c) high sulfur concentrations in rain over "remote" European stations are now largely attributed to long-range transport of man-made sulfur rather than to natural sources (Granat et al. (ref. 2)). It

follows that the natural source strength is small (<10 percent) compared with man-made emissions over northwestern Europe (Rodhe (ref. 3)). By inference, this also holds for northeastern United States and southeastern Canada.

(3) Removal: Dry and wet removal rates are of comparable magnitude and the overall average removal rate is about 2 to 3 percent/hour. Dry removal rate is controlled both by the stomatal resistance of the vegetation and by the atmospheric resistance to mixing (Garland (ref. 27) and Hales (ref. 28)).

(4) Transformations: The average oxidation rate over the lifetime of SO_2 is about 1 to 2 percent/hour as obtained by fitting the rate constants in regional-scale models to European monitoring data (Eliassen (ref. 29)). In plumes of a midwestern United States power plant, the daytime conversion rate was measured to be 1 to 4 percent/hour and <0.5 percent/hour at night (Husar et al. (ref. 19)). Laboratory simulations of gas-phase-controlled SO_2 conversion in the presence of oxidizing radicals (Calvert et al. (ref. 6) and Eggleton and Cox (ref. 8)) come "embarrassingly close" (Friedlander (ref. 30)) to the 1 to 2 percent/hour daily average conversion rate. The contribution of liquid-phase oxidation is not well established, but it is thought to be significant (Beilke and Gravenhorst (ref. 9), Hegg and Hobbs (ref. 31), and Workshop (ref. 4)).

(5) Aerosol: About 20 to 50 percent of the SO_2 converts in the atmosphere to aerosol, and the product has been positively identified to be SO_4^{2-} ion (Stevens et al. (ref. 32)). The main cations are NH_4^+ or H^+ depending on the air mass history (Brosset (ref. 33) and Charlson et al. (ref. 34)). The sulfate (except in marine aerosol) is in the submicrometer size range (Whitby et al. (ref. 20), Jaenicke (ref. 35), Newman (ref. 36), and Stevens et al. (ref. 32)). For gas-phase-controlled conversion, the aerosol growth kinetics is qualitatively understood (Friedlander (ref. 30), Whitby et al. (ref. 20), and Workshop (ref. 4)).

(6) Residence times: The turnover (average residence) times are about 1 day for SO_2 ; 3 to 5 days for SO_4^{2-} , and about 2 to 3 days for sulfur (Rodhe (ref. 3) and Workshop (ref. 4)). The corresponding transport distances may be estimated by taking a speed of about 500 km/day.

(7) Large projects: Large-scale monitoring networks (Ottar (ref. 12), Perhac (ref. 13), Whelpdale (ref. 37), and MacCracken (ref. 14)) in conjunction with long-range transport models (Eliassen (ref. 29) and Fisher (ref. 38)) are useful tools for the estimation of regional-scale (order of 1000 km) distribution and budgets. On the other hand, mesoscale or plume studies (Wilson (ref. 18)) elucidate the diurnal pattern and other details of transport, transformation, and removal processes. A continuous exchange of findings and some coordination of these projects is desirable.

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TABLE I.- DEPOSITION VELOCITIES

[From Workshop (ref. 4)]

(a) Over vegetation

Vegetation		Height, m	Range of deposition velocity, cm/sec	Typical deposition velocity, cm/sec (a)
Height	Example			
Short	Grass	0.1	0.1 to 0.8	0.5
Medium	Crops	1.0	0.2 to 1.5	.7
Tall	Forest	10.0	0.2 to 2.0	Uncertain

^aThese values were obtained in a humid climate. Much smaller values are likely in arid climates.

(b) Over soil^b

Soil type	pH	State	Range of deposition velocity, cm/sec	Typical deposition velocity, cm/sec
Calcareous	≥7	Dry	0.3 to 1.0	0.8
Calcareous	≥7	Wet	0.3 to 1.0	.8
Acid	≈4	Dry	0.1 to 0.5	.4
Acid	≈4	Wet	0.1 to 0.8	.6

^bAs yet no information is available to assess deposition velocity on desert sand or lateritic soils.

TABLE II.- REPRESENTATIVE ANNUAL AVERAGE WET AND DRY DEPOSITION RATES

[Workshop (ref. 4)]

Location		Excess precipitation sulfate concentration, mg S/liter	Wet deposition rate, g S/m ² -yr	Dry deposition rate, g S/m ² -yr
Heavily industrialized areas	North America	3 to ?	^a 0.1 to 3	?
	Europe	3 to 20	2 to 4	3 to 15
Rural	North America	0.5 to 2	0.1 to 2	0.2 to 2.6
	Europe	0.5 to 3	0.2 to 2	0.5 to 5.0
Remote	North Atlantic Ocean	0.2 to 0.6	1 to 3	0.04 to 0.4
	Other Oceans	0.04	^a 0.01 to 0.2	<0.1
	Continents	0.1	^a 0.01 to 0.5	0.4

^aLow deposition rates result from low precipitation.

TABLE III.- PARAMETER VALUES APPLIED IN CALCULATIONS WITH THE
LAGRANGIAN DISPERSION MODEL

[The same values have also been applied in the calculations
with the trajectory model (OECD (ref. 11))]

Parameter	Definition	Value
α	Part of sulphur emission deposited locally	0.15
β	Part of sulphur emission transformed directly to sulphate	0.05
k	Decay rate SO_2 $\begin{cases} \text{Rain} \\ \text{Dry} \end{cases}$	$4 \times 10^{-5} \text{ sec}^{-1}$ $1 \times 10^{-5} \text{ sec}^{-1}$
k_t	Transformation rate $\text{SO}_2 \rightarrow \text{SO}_4$	$3.5 \times 10^{-6} \text{ sec}^{-1}$
κ	Loss rate SO_4	$4 \times 10^{-6} \text{ sec}^{-1}$
h	Mixing height	1000 m

1973 U.S. SO_x EMISSIONS

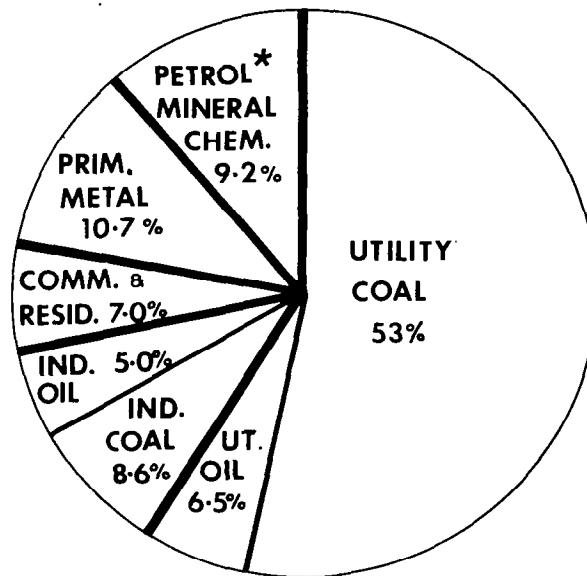


Figure 1.- Sources of SO₂ in the United States, 1973. Petrol mineral chem. section includes 2 percent attributed to transportation. (U.S. Environmental Protection Agency (ref. 1).)

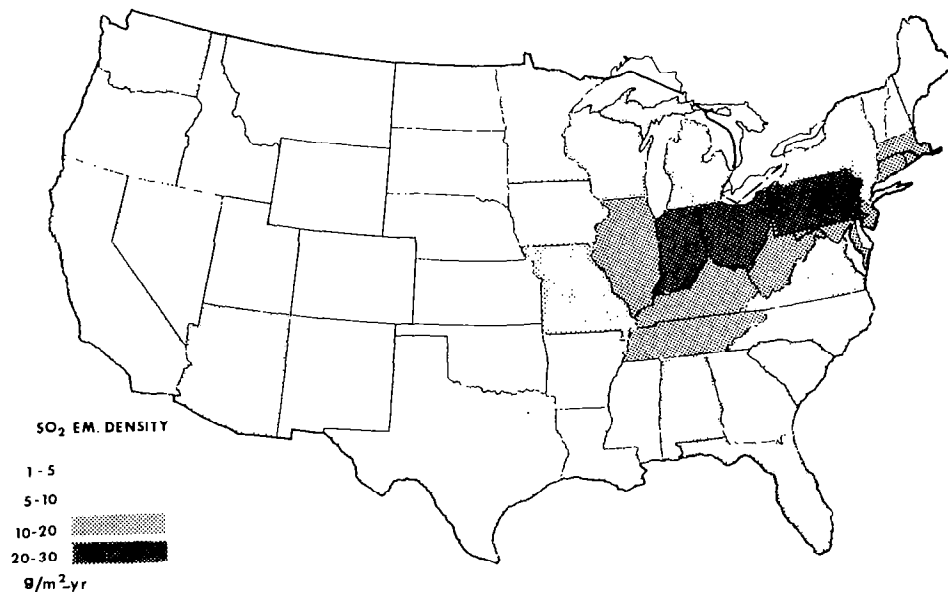


Figure 2.- SO₂ emission density by state. (U.S. Environmental Protection Agency (ref. 1).)

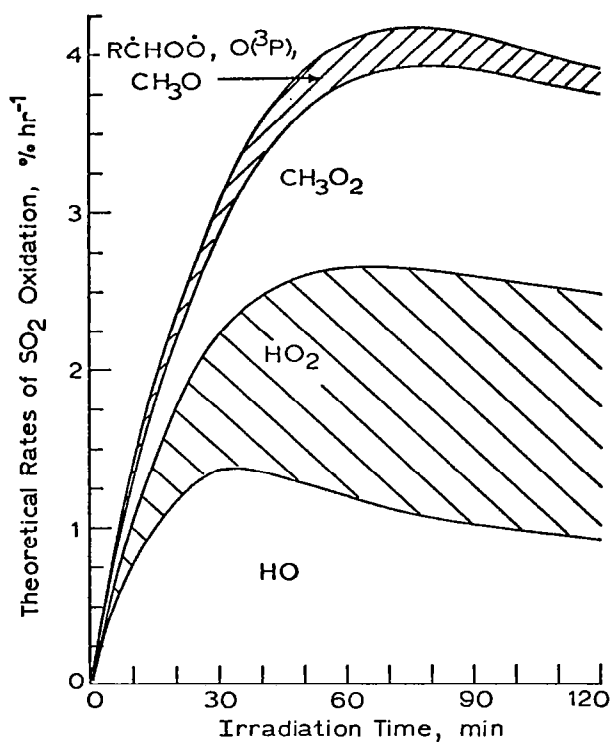


Figure 3.- Theoretical rate of attack of various free radical species on SO_2 for a simulated sunlight-irradiated (solar zenith angle = 40°) polluted atmosphere. Initial concentrations (ppm): $[\text{SO}_2] = 0.05$, $[\text{NO}] = 0.15$, $[\text{NO}_2] = 0.05$, $[\text{CO}] = 10$, $[\text{CH}_4] = 1.5$, $[\text{CH}_2\text{O}] = 0$, $[\text{CH}_3\text{CHO}] = 0$; relative humidity, 50 percent (25°C). (From Calvert et al. (ref. 6) with permission from Pergamon Press, Ltd.)

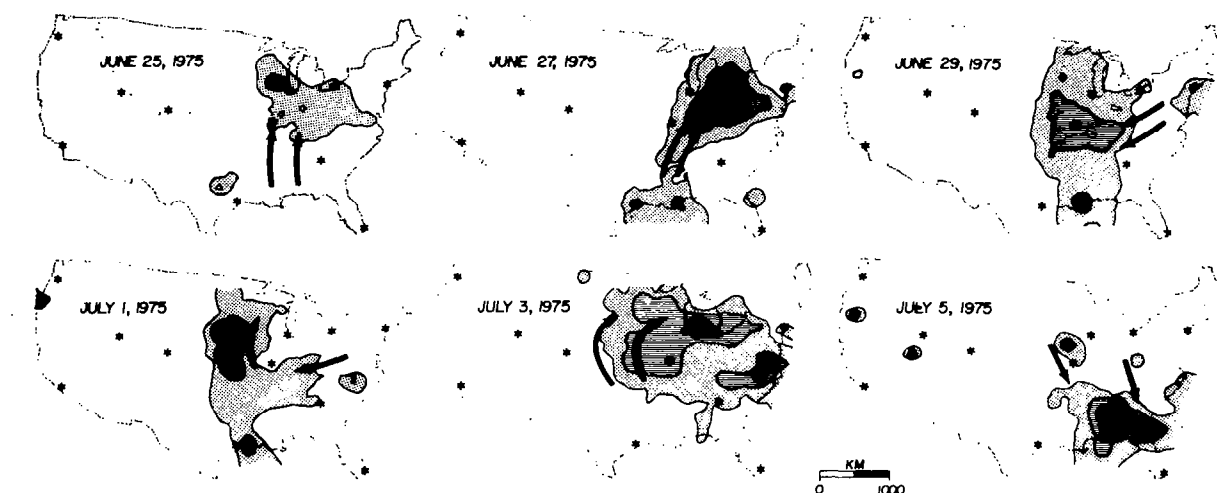


Figure 4.- Maps of noon visibility over the continental United States between June 25 and July 5, 1975. Contours are plotted for extinction coefficients of 4×10^{-4} , 6×10^{-4} , and $8 \times 10^{-4} \text{ m}^{-1}$, corresponding to visual ranges of 10 to 6 km (light shade), 6 km (medium shade), and 5 km (black shade). (From Husar et al. (ref. 16).)

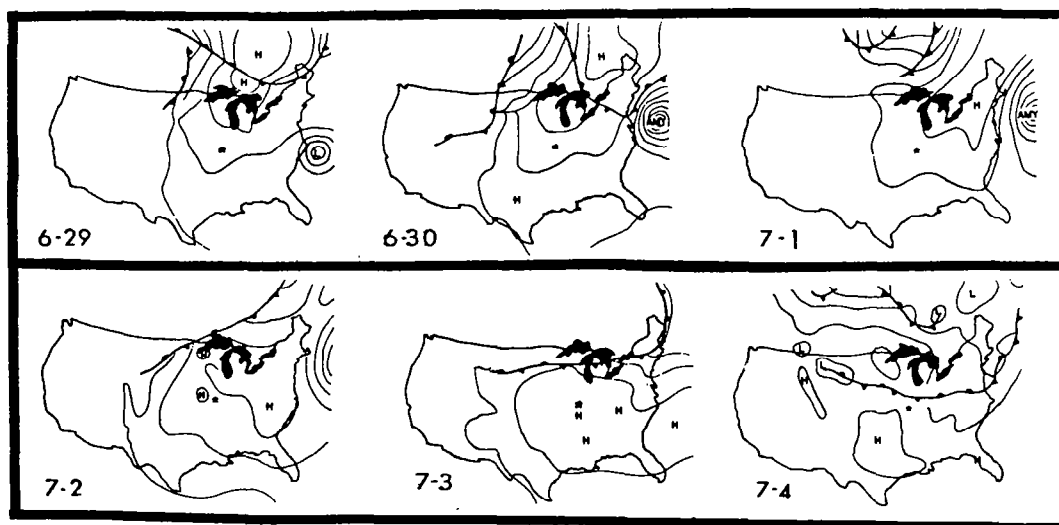
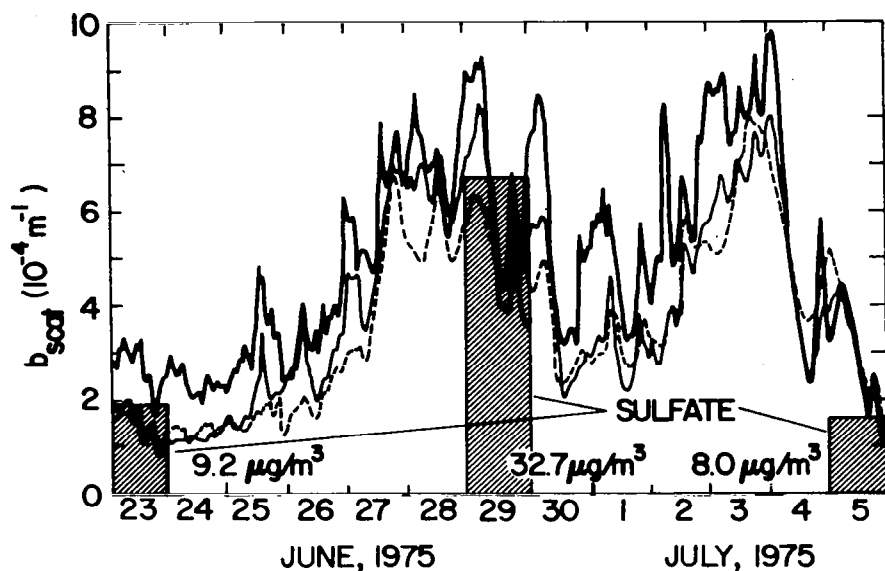
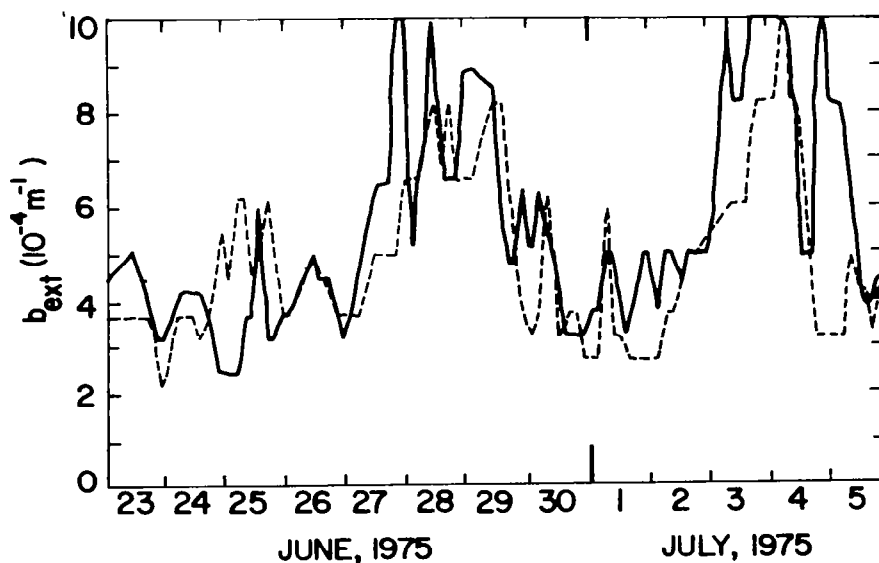


Figure 5.- Daily weather maps for June 29 to July 4, 1975. (From Husar et al. (ref. 16).)

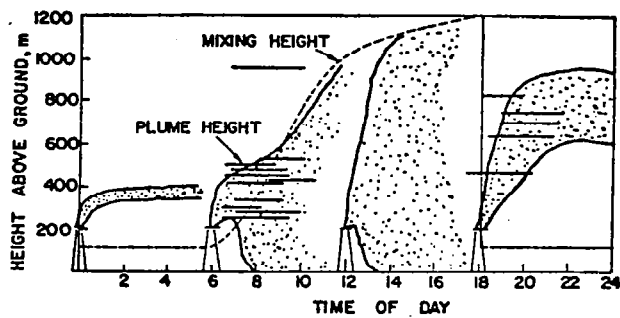


(a) Light scattering coefficient (b_{scat}) recorded by St. Louis County Department of Health near downtown (— station 4), near the western city limits (— station 9), and at background location (--- station 6, 38 km west of city). Nephelometers located north and south of the city show similar b_{scat} patterns (not shown).

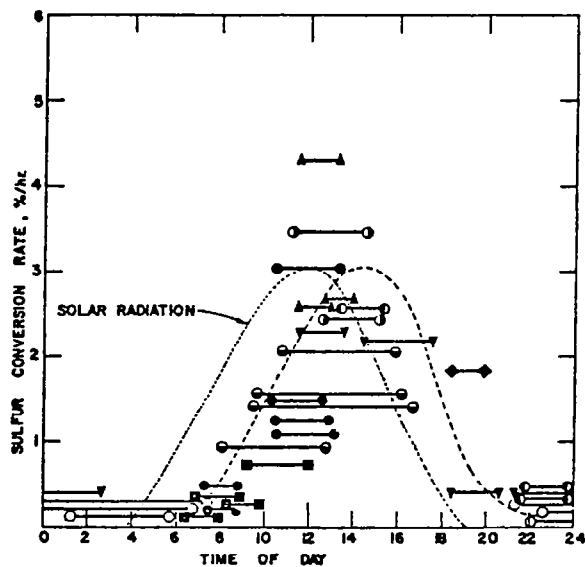


(b) Extinction coefficients (b_{ext}) calculated by $b_{\text{ext}} = 3.92/V$ from observations of visible range V at St. Louis Lambert Airport (—) and at Springfield, Illinois, airport (---) located 150 km northeast of St. Louis.

Figure 6.— Visibility observations near St. Louis for June 29 to July 4, 1975. (From Husar et al. (ref. 16).)

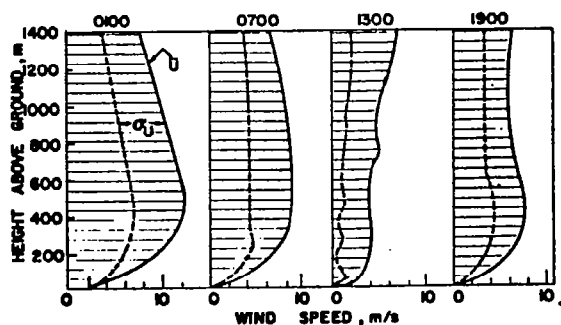


(a) Diurnal pattern of plume dispersion.

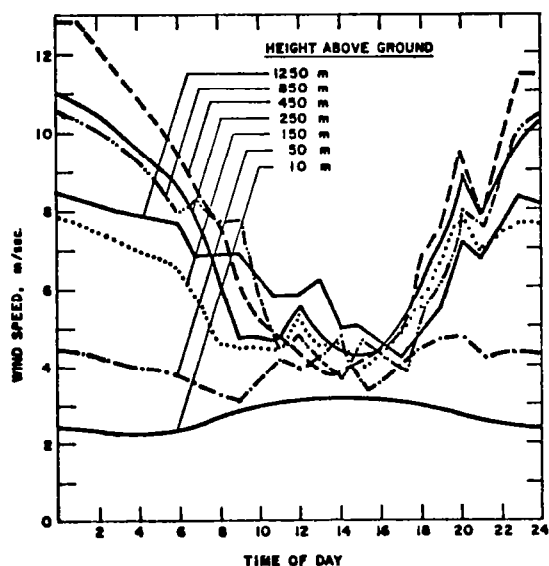


(b) Conversion rate.

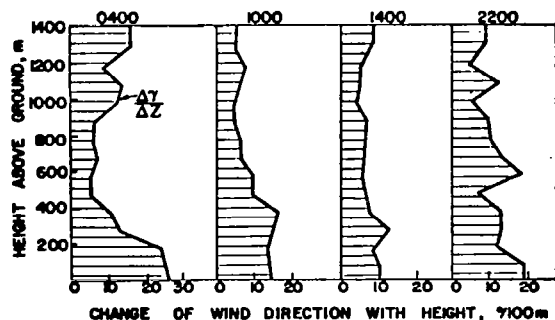
Figure 7.- Diurnal pattern of plume behavior.
(From Husar et al. (ref. 19).)



(a) Vertical profiles of velocity for 0100, 0700, 1300, and 1900 CDT releases. Note appearance of nocturnal jet at about 500 m and uniform low wind speed at midday.



(b) Diurnal pattern of wind speed at seven different heights.



(c) Change of wind direction with height. Evidently, nocturnal jet has little "veer," less than $8^\circ/100$ m on the average.

Figure 8.- Wind data obtained from hourly releases by RAPS balloon sounding network, averaged for July 1976. (From Husar et al. (ref. 19).)

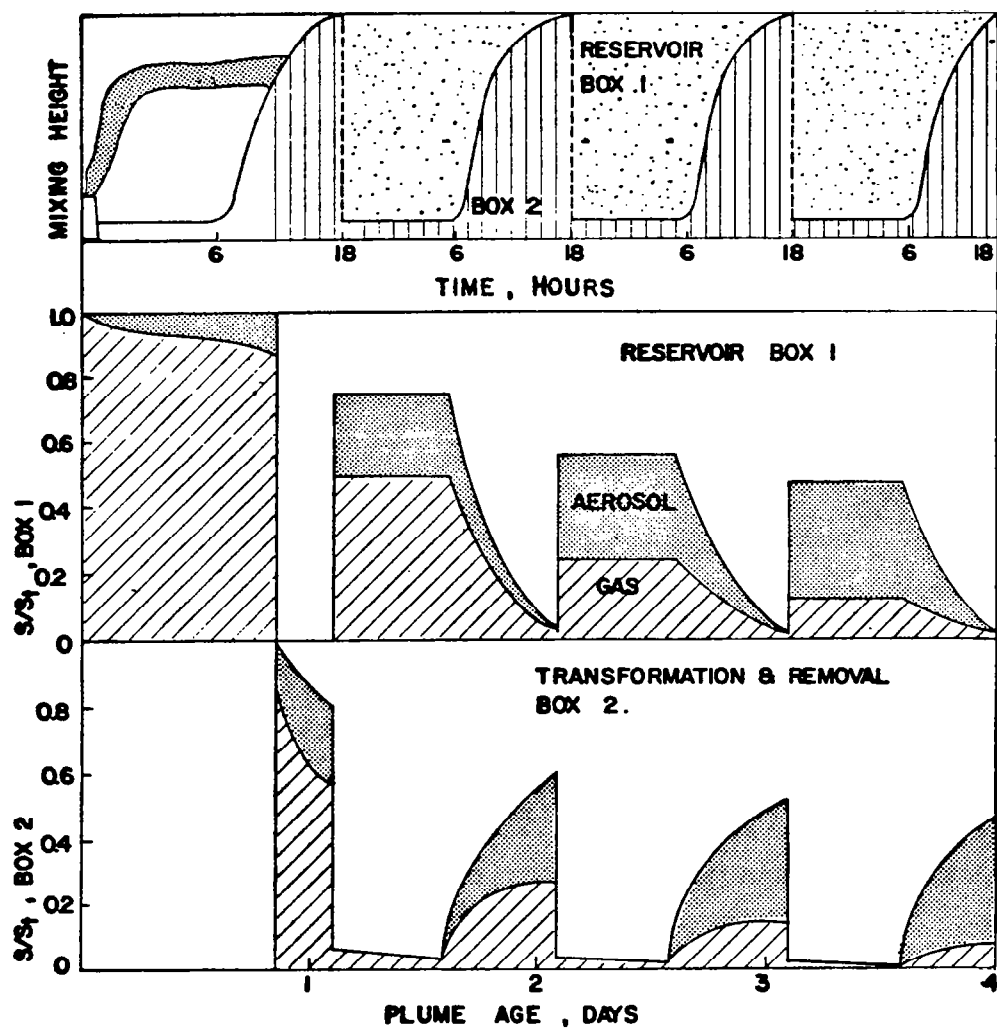


Figure 9.- Schematics of plume transition from the quiescent reservoir to mixing, transformation, and removal regime (top), gaseous and particulate sulfur in the reservoir box (center), and removal regime (bottom).

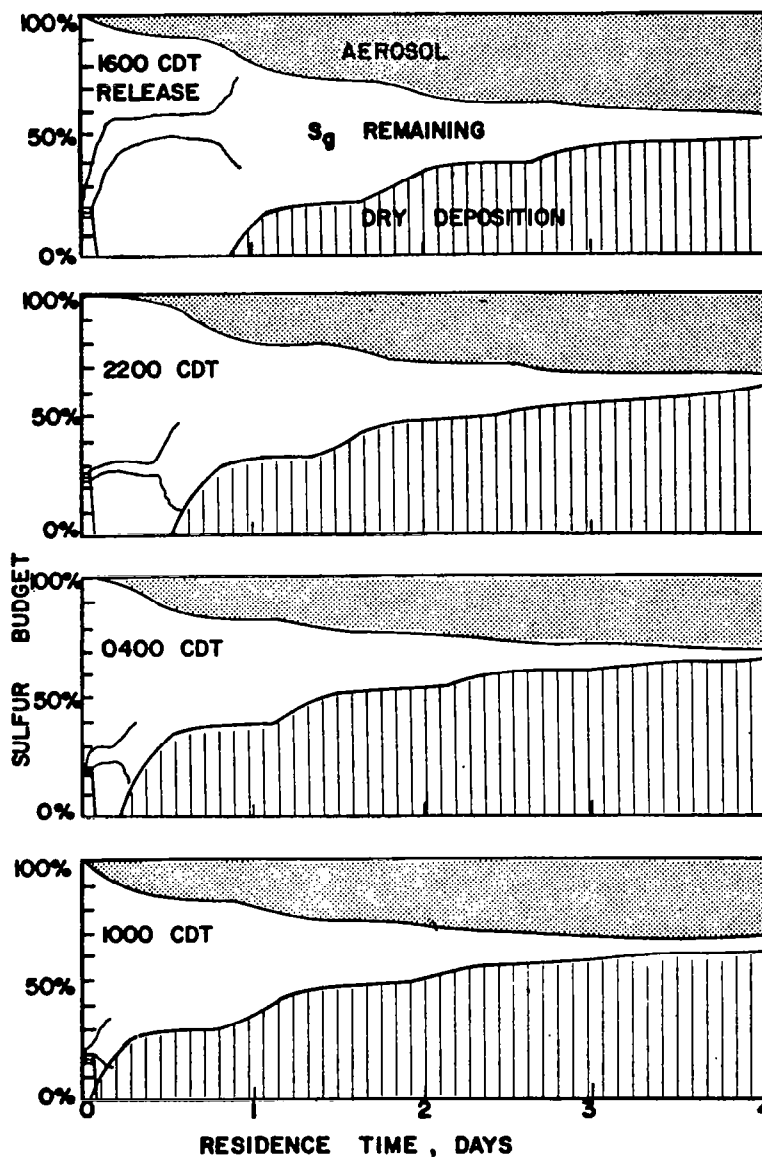
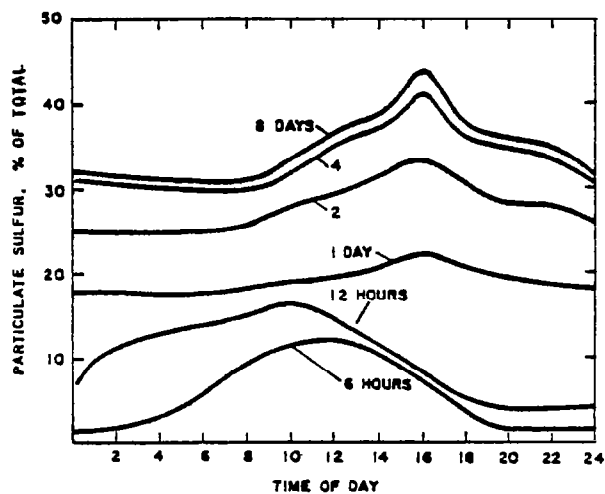
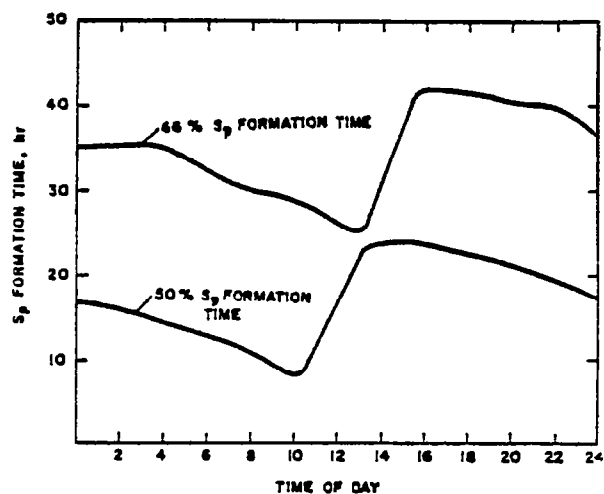


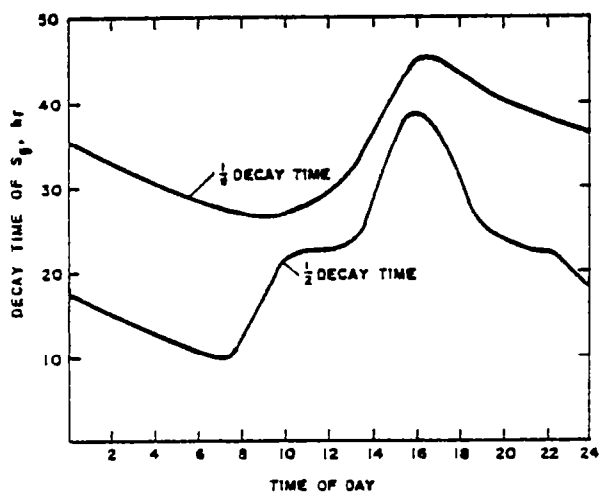
Figure 10.- Sulfur budget over 4 days for power plant emission obtained from two-box model, for four emission times.



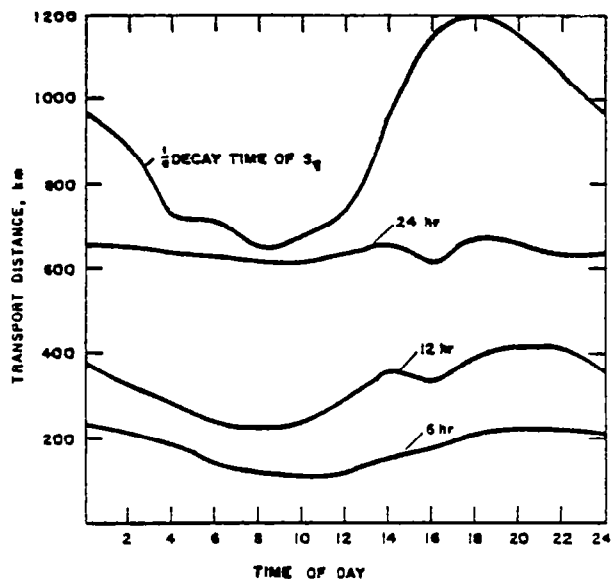
(a) Particulate sulfur fraction for different plume ages.



(b) Particulate sulfur formation time.



(c) S_g decay time.



(d) Transport distance.

Figure 11.- Results of model calculations to explore role of emission time.